Supplementary Information for

Accessing nanoscopic polarization reversal processes in an organic ferroelectric thin film

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Deceased on April 24th, 2018.

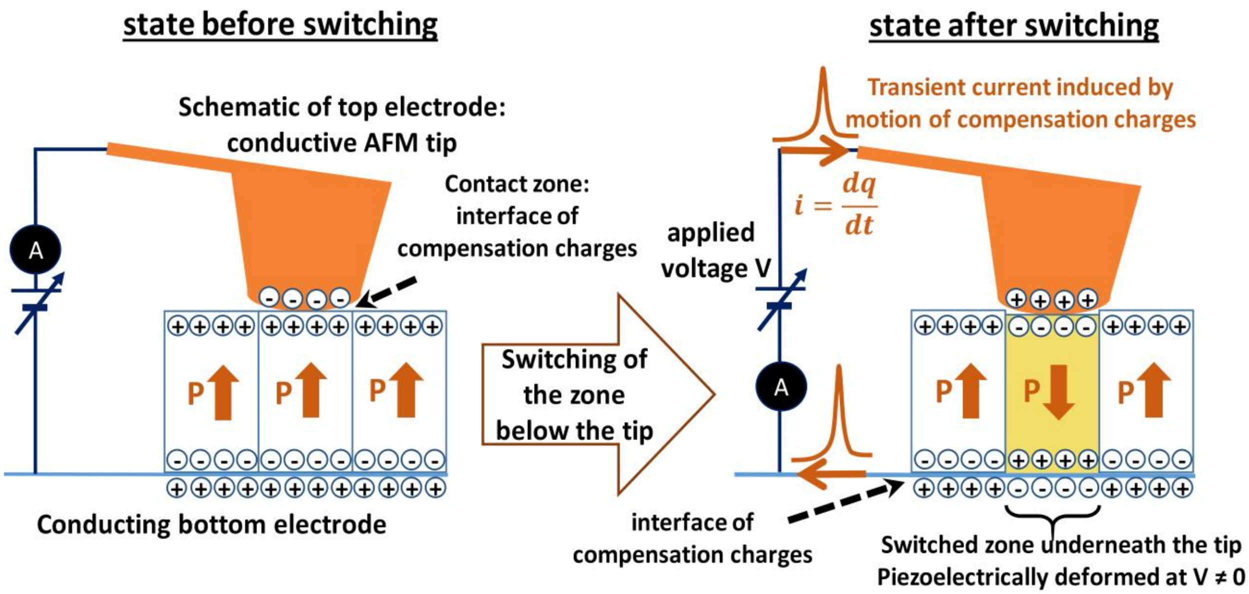

Figure S1. Schematics of polarization switching event. The upward polarization of the central zone in the initial state is reversed by the application of voltage via the AFM tip in contact with the zone. The switching results in the flow of charges in the circuit to compensate the new polarization charges that appear at the surfaces of the switched zone after the polarization reversal. This generates current peaks (*i=dq/dt*) whose shape depends on the kinetics of the switching process and the associated compensation process.

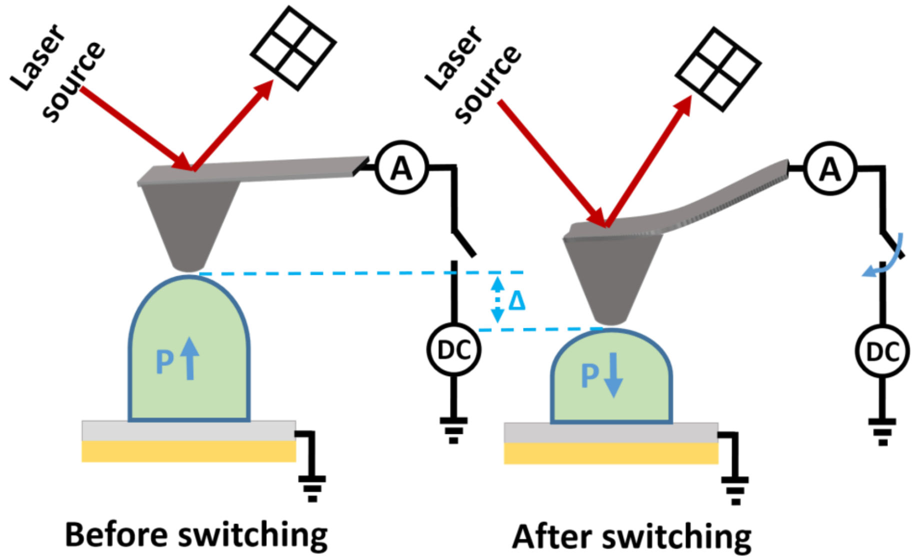

Figure S2. Schematics of the origin of piezoelectric electromechanical strain response during a ferroelectric switching event. Application of an electric field to a nanoscopic ferroelectric region results in the mechanical deformation of the region via the inverse piezoelectric effect. Along the direction of the electric field, the deformation can be expansive or compressive, depending on whether the electric field is aligned parallel or anti parallel to the nanoscopic polarization, respectively. During a nanoscopic switching current spectroscopy, the deflection of the laser beam (reflected from the cantilever) due to the polarization reversal-induced cantilever deformation is captured by the position sensitive crossed photodetector. The strain response or the electromechanical deformation (Δ) of the nanoscopic ferroelectric region is proportional to the change in the cantilever deformation during the polarization reversal/switching event.

Figure S5 presents the individual strain response curves of all the 11 measurements corresponding to figure 3 in the main text, where we see that for many of the curves on the positive side of the applied voltage, no sharp jump is visible on the strain response curves; rather a very gradual jump is evident. On the negative side, however, the jump on every single strain response curve is sharp. This is consistent with the multi-stepped or gradual reversal kinetics on the positive

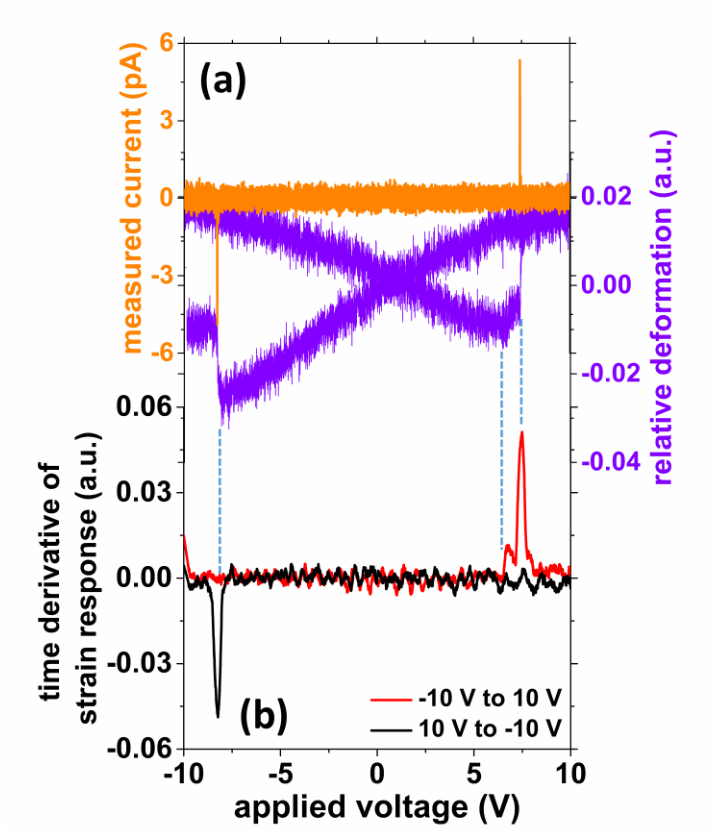

Figure S3. Detailed view of the measured current and the strain response corresponding to figure 2. (a) shows the measured current (orange curve) superposed on the strain response (blue curve). (b) shows the first order time derivative of the strain response curve smoothened by Savitzky-Golay filter with points of window = 500. Strain response curve in (a) is purposefully shifted by an appropriate magnitude for a better comparison with the current peaks. Dashed lines indicate the position (negative bias) and spread (positive bias) of the jump on the strain response curve.

side of the applied voltage. This becomes more evident when time derivative of all the strain response curves are plotted (Figure S6). A gradual or stepwise process results in a broad peak or multiple peaks, respectively, in the derivative spectrum, at positive bias (red curve) for many curves in figure S6, for example. Whereas, a single or narrow peak is indicative of a sharp reversal event, at negative bias (black curve) in figure S6, for example.

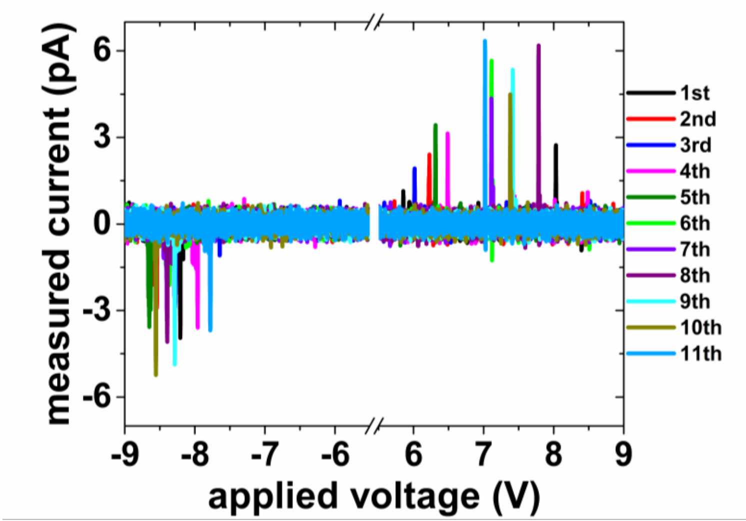

Figure S4. Ensemble of I-V spectroscopic curves corresponding to figure 3. Repeated I-V spectroscopies were performed on the same nanoscopic region with a time interval of 100 μs between each two successive measurements. Each color represents one spectroscopic measurement as indicated by the corresponding index.

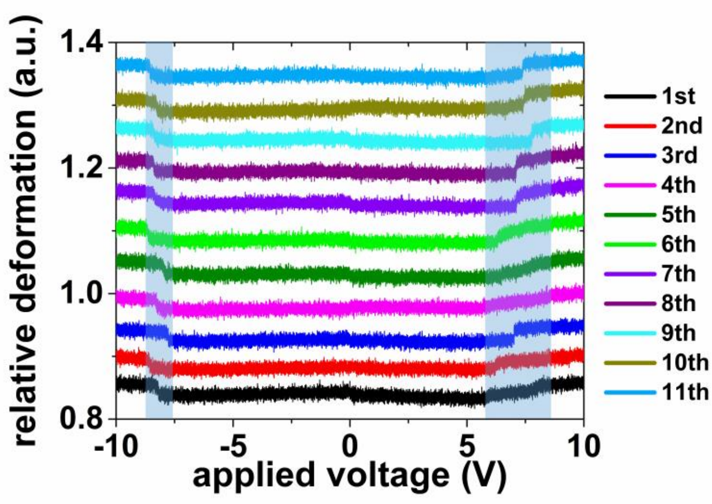

Figure S5. Strain response curves of switching spectroscopies of figure 3. For the sake of clarity, only the branches that contain the polarization switching related jumps are shown for each of the curves. Colors represent the sequence of individual spectroscopic measurements. The curves are shifted by appropriate magnitude for clarity. The blue shades show the ranges of applied voltage over which jumps on the deformation curves take place on either side of the applied voltage.

Polarization switching current is an important measurement parameter when it comes to

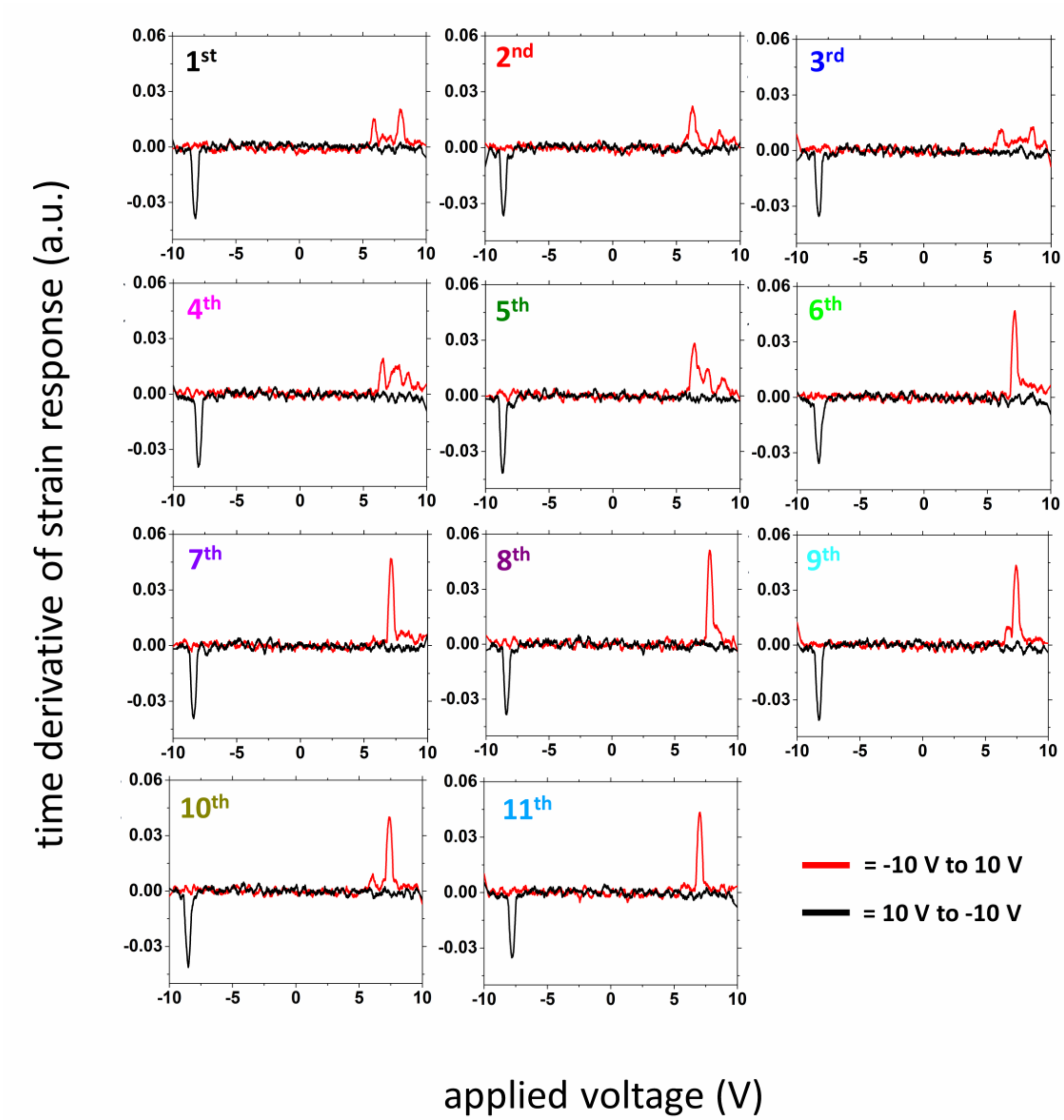

Figure S6. Time derivative plots of strain response ensemble corresponding to the spectroscopic I-V measurements of figure 3. Curves are smoothened by Savitzky-Golay filter with points of window = 600. The colored indices correspond to the sequence of individual measurements. The correct way to get information on the reversal kinetics would be to study the spread of the peaks, not the heights, for the magnitude of deformation is not known to be constant for the entire ensemble of measurements.

the characterization of ferroelectric materials. While at the macroscale the switching current is widely used to record hysteresis loops and measure the polarization, at the nanoscale however, the switching currents can evidence fast polarization reversal events, where gradual reversals can be missed easily due to the presence of background noise. The polarization values deduced from the switching currents may be significantly biased due to background noise and instrument limitations and thus result in a severe distortion of the hysteresis loops. The shape of the hysteresis loop measured by PFM phase is not affected by these problems but depends on the AC signal applied to the tip. In any case, the reversal at the nanoscale is, in essence, stochastic in terms of the reversal kinetics and the applied voltage at which it takes place. Thus, one has to be cautious before deducing material properties from a single or a limited number of measurements. For a ferroelectric memory element for instance, the voltage required to reverse the polarization with a given probability must be determined by numerous trials.

Raw data and background subtraction:

Figure S7a shows the raw I-V curve corresponding to figure 2a in the main text. The background is a sloped straight line which can be removed by subtracting a reference I-V curve from the raw curve. This reference curve is obtained by taking an I-V measurement with the tip far away from the sample, while keeping all experimental conditions and parameters unchanged. An example of a reference curve obtained with the tip far away from the sample (for different measurement parameters than figure S7a) is shown in figure S7b, where the linear current background is evident. It should be noted that there is no leakage current present in our measurements for the range of voltage applied. This makes it relatively easier to subtract the current background. Further, the possibility of successful polarization switching without leakage current makes Croconic Acid an interesting candidate material for nanoscopic ferroelectric devices.

As the nature of the reference curve may depend on the I-V measurement parameters, such as the ramping speed, it is not practical to obtain the reference curve for each I-V measurement.

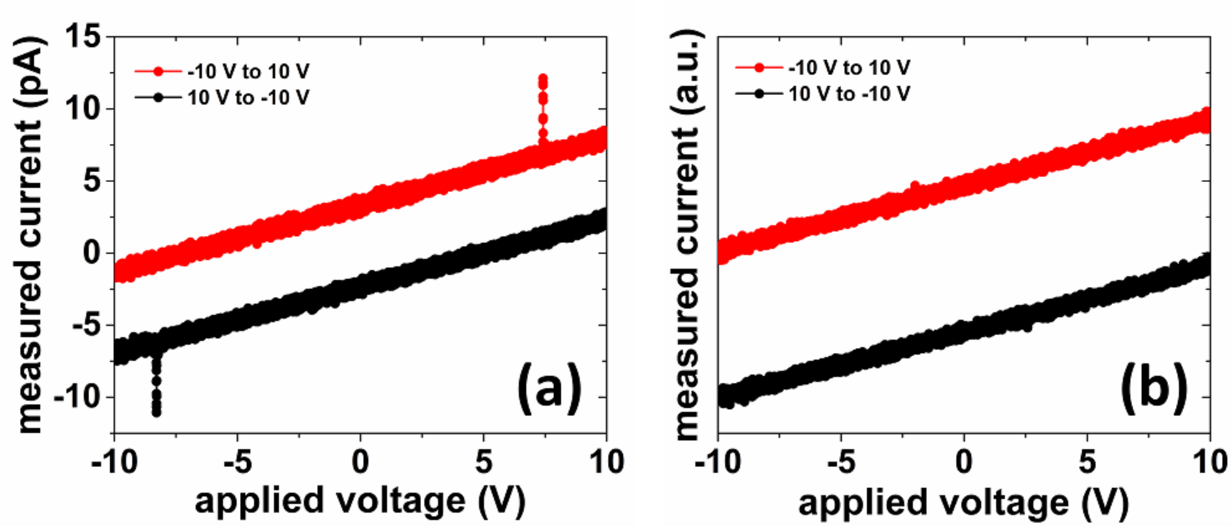

Figure S7. Raw data for switching current spectroscopy measurements corresponding to figure 2a in the main text.

Alternatively, a simpler background subtraction method can be employed to remove the background which is essentially linear. To do so, a linear fit to the raw I-V data in the voltage range far away from the switching biases is approximated. This is extrapolated to span over the entire range of measurement voltage and then the resulting straight line is subtracted from the raw I-V data. To make the background subtraction more accurate, algorithms like asymmetric least square fitting can be employed to generate a background curve away from the switching biases to be subtracted from the raw data, which can remove any minor non linearities in the current background. It must be noted that in figure S7a there are 20,000 data points for the red and the black curve each and a measurement time of 100 µs is associated to each data point.

Choice of ramping speed:

An important parameter for I-V measurement on a ferroelectric material is the ramping speed of the applied voltage, as it may substantially influence the shape of the hysteresis loop, the kinetics of polarization reversal and the shape of the switching current peaks. The ramping speed is essentially dependent on the number of measurement data points and the sampling factor for each measurement. Large number of data points results in a slower ramp but is essential to observe an accurate switching current peak, especially in the case of fast polarization reversal. Similarly, while smaller sampling factor increases the noise level in the measured current, large sampling factor may result in oversampling issues. Further, as a large sampling factor increases the measurement time for each data point, this may result in the failure to capture the peaks accurately if reversal kinetics is very quick. Thus, the choice of ramping speed, which is limited by the minimum possible measurement time of the instrument, acceptable noise level and the rate of polarization reversal in the material under study, must be optimized to obtain accurate switching current peaks. For example, in the current work, all the I-V measurements are carried out with a measurement time of 100 µs per data point and 1000 data points per 1 V. This provides a balanced ramping speed to detect the switching current peaks with reasonably low levels of noise in the current measurement.